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FLUORINE GAS GENERATING APPARATUS
[FUSSO GASU HASSEI SOUCHI]

TETSURO TOJO, et al.

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INVENTOR(S)	(72):	Tetsuo Tojo, et al.
APPLICANT(S)	(71):	Toyo Tanso Co., Ltd.
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Specification

FLUORINE GAS GENERATING APPARATUS

Technical Field

The present invention relates to a fluorine gas generating apparatus and, in particular, to a fluorine gas generating apparatus producing a high-purity fluorine gas with an extremely low level of impurities for use in semiconductor manufacturing processes and the like.

Technical Background

Fluorine gas is an indispensable basic gas used, for instance, in the field of semiconductor manufacture. Also, while fluorine gas may be used on its own, there is a rapidly growing demand for nitrogen trifluoride gas (referred to as "NF_3 gas" below) synthetically prepared from fluorine gas and utilized as a semiconductor cleaning gas or as a dry etching gas. Further, gases such as neon fluoride gas (referred to as "NeF gas" below), argon fluoride gas (referred to as "ArF gas" below), krypton fluoride gas (referred to as "KrF gas" below), etc. are lasing gases used for excimer lasers employed in the

patterning of semiconductor integrated circuits, and gas mixtures made up of noble gases and fluorine gas are often used as raw materials for their production.

Fluorine gas or NF_3 gas used in semiconductor manufacture etc. has to be a high purity gas containing a low level of impurities. Further, at semiconductor manufacturing sites, etc., a necessary amount of such gas is commonly taken from a gas cylinder filled with fluorine gas. Accordingly, selecting a storage location for the gas cylinders, ensuring the safety of the gas, maintaining the purity of the gas, and other management issues are extremely important. Furthermore, with the recent rapid increase in the demand for NF_3 gas, there are certain problems in terms of supply and, to a certain extent, problems in terms of overstocking. In view of these problems, installing on-demand, on-site equipment for fluorine gas generation at the location of use is more preferable than handling high-pressure fluorine gas.

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Fluorine gas is normally produced in an electrolytic cell, such as the one illustrated in FIG. 9. Ni, Monel™, carbon steel, etc. are typically employed as the material, from which the body of the electrolytic cell 201 is made. Furthermore, in order to prevent the generated hydrogen gas

and fluorine gas from mixing, the bottom of the cell is fitted with a base plate 212 made of polytetrafluoroethylene, etc. The body of the electrolytic cell 201 is filled with a molten salt mixture containing potassium fluoride and hydrogen fluoride (referred to as th e"KF-HF system" below), which forms an electrolytic bath 202. In addition, the cell is divided into an anode chamber 210 and a cathode chamber 211 by a skirt 209 formed from Monel and the like. Fluorine gas is produced electrolytically by applying a voltage between a carbon or nickel (referred to as Ni below) anode 203 housed in the anode chamber 210 and a Ni cathode 204 housed in the cathode chamber 211. It should be noted that the produced fluorine gas is discharged from a generating port 208 and the hydrogen gas generated on the cathode side is discharged from a hydrogen gas discharge port 207. Incidentally, the problem is that it has been difficult to obtain high purity fluorine gas due to the admixture of carbon tetrafluoride gas (referred to as "CF_4 gas" below) generated during electrolysis or hydrogen fluoride gas (referred to as "HF gas" below) evaporated from the electrolytic bath.

Thus, it is an object of the present invention to provide a fluorine gas generating apparatus capable of generating high purity fluorine gas in a stable manner.

Disclosure of Invention

Intended to solve the above-mentioned problems, the fluorine gas generating apparatus of the present invention, which is a fluorine gas generating apparatus used for producing high purity fluorine gas by electrolysis of a molten salt mixture containing hydrogen fluoride, comprises: an electrolytic cell divided into an anode chamber and a cathode chamber by a partition wall, and a pressure maintaining means, which supplies gas to the above-mentioned anode chamber and the above-mentioned cathode chamber, respectively, in order to maintain the interior of the above-mentioned anode chamber and the above-mentioned cathode chamber at a predetermined pressure.

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The pressure maintaining means maintains the interior of the anode chamber and cathode chamber at a constant pressure at all times. For this reason, a rare gas serving as a carrier gas can be introduced therein to quickly achieve a predetermined fluorine concentration and flow rate. In particular, after the startup of the electrolytic

cell, it can be promptly brought to a state that permits use of the gas. Futher, maintaining the interior of the anode chamber and cathode chamber at a predetermined pressure makes it possible to prevent entry of air etc. from the outside and permits stable generation of high purity fluorine gas. It should be noted that the expression “maintaining at a predetermined pressure”, as used in the present invention, is assumed to include states, in which there is no pressure differential relative to the external environment (e.g. use at atmospheric pressure).

Further, the fluorine gas generating apparatus of the present invention, which is a fluorine gas generating apparatus used for producing high purity fluorine gas by electrolysis of a molten salt mixture containing hydrogen fluoride, comprises: an electrolytic cell divided into an anode chamber and a cathode chamber by a partition wall; a pressure maintaining means, which supplies gas to the above-mentioned anode chamber and the above-mentioned cathode chamber, respectively, in order to maintain the interior of the above-mentioned anode chamber and the above-mentioned cathode chamber at a predetermined pressure; a controlled atmosphere cabinet housing the above-mentioned electrolytic cell; and a filter, which is housed in the above-mentioned cabinet and removes particles from the

fluorine gas generated by the above-mentioned electrolytic cell.

This makes atmosphere control around the electrolytic cell possible and allows for reliably preventing the invasion [*sic; typographical error, "entry". - trans.*] of carbon dioxide gas into the electrolytic cell. As a result, the production of CF_4 gas produced by the reaction between the fluorine gas and carbon dioxide gas can be minimized and a high purity fluorine gas can be obtained. Further, even if a fluorine gas leak from the electrolytic cell does occur, there is no concern about it leaking outside. In addition, particles generated by entrainment from the electrolytic bath during electrolysis can be reliably removed by the filter. As herein described, the filter will preferably be resistant to corrosion by fluorine gas and will be made, for example, from sintered Monel, sintered Hastelloy, and the like. Additionally, the cabinet that houses the electrolytic cell will preferably possess resistance to corrosion by fluorine gas and will be formed, for example, from vinyl chloride and the like or a metal such as carbon steel.

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Furthermore, in the fluorine gas generating apparatus of the present invention, at least either one of the above-

mentioned anode chamber and the above-mentioned cathode chamber of the above-mentioned electrolytic cell is equipped with a liquid surface sensing means for sensing the uppermost level and lowermost level of liquid level fluctuation of the molten salt.

Thus, the height of the liquid surface in the electrolytic bath can be determined even when the interior of the electrolytic cell cannot be visually observed. For this reason, the level of the electrolytic bath can be maintained constant at all times and the electrolytic bath can be prevented from backflowing, etc. Further, placing the liquid surface sensing means in operative association with an electrode power supply control means allows for the electrolysis to be halted whenever there is an abnormal liquid surface level in the electrolytic bath.

Additionally, in the fluorine gas generating apparatus of the present invention, the above-mentioned pressure maintaining means is equipped with a solenoid valve that is opened and closed based on the sensing results of the above-mentioned liquid surface sensing means for supplying or discharging gas to and from the interior of the above-mentioned anode chamber and the above-mentioned cathode chamber.

The supply or discharge of the gas to and from the interior of the anode chamber and/or cathode chamber can be carried out automatically based on the sensing results of the sensing means in accordance with the height of the liquid surface of the electrolytic bath. For this reason, the height of the liquid surface in the electrolytic bath can be maintained constant at all times, thereby permitting stable fluorine gas generation.

Further, in the fluorine gas generating apparatus of the present invention, the molten salt mixture containing hydrogen fluoride is a KF-HF system and the apparatus is equipped with a temperature regulating means for regulating the temperature of the above-mentioned molten salt mixture containing hydrogen fluoride.

The temperature of the molten salt mixture in the electrolytic cell during electrolysis can be maintained at a constant temperature at all times. For this reason, fluorine gas can be produced in an efficient manner.

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Further, in the fluorine gas generating apparatus of the present invention, the gas supplied by the above-mentioned pressure maintaining means is a rare gas.

Gas mixtures with various mixing ratios can be obtained by diluting the generated gas with gases such as

neon gas (Ne gas), argon gas (Ar gas), krypton gas (Kr gas) and the like and used as lasing gases for excimer lasers employed in the patterning of semiconductor integrated circuits.

Further, in the fluorine gas generating apparatus of the present invention, the anode and cathode disposed in the above-mentioned anode chamber and the above-mentioned cathode chamber are made of nickel.

Since a Ni anode is used, the dislodgment of carbon particles, which occurs when electrolysis is performed using carbon electrodes, is prevented. In this manner, no CF_4 admixture takes place due to reactions between carbon and fluorine gas, and a high purity fluorine gas can be produced. In addition, the anode effect, i.e. the polarization phenomenon, which is characteristic of carbon electrodes, can be prevented as well. Furthermore, when Ni is used for the cathode as well, the hydrides and oxides generated on the surface of the Ni reduce its surface energy below that of an iron cathode, the bubbles of the generated hydrogen gas become larger and it can be prevented from mixing with the fluorine gas. Additionally, this makes it possible to shorten the distance between the anode and cathode and permits miniaturization of the electrolytic cell.

Further, in the fluorine gas generating apparatus of the present invention, the above-mentioned electrolytic cell is formed from metal.

The use of metals of high strength and high airtightness, such as Ni, Monel, pure iron, and stainless steel for the joints and body of the electrolytic cell allows for preventing gas leakage etc. from the electrolytic cell. For example, leakage of helium gas can be avoided even when the interior of the electrolytic cell has a helium gas atmosphere under a pressure that is 0.1 MPa higher than atmospheric pressure.

Further, in the fluorine gas generating apparatus of the present invention, the above-mentioned electrolytic cell is cylindrical in shape.

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The temperature regulating means can uniformly heat the electrolytic cell around its entire perimeter. Further, since the electrode arrangement is concentrical in shape, the distribution of the electrical current inside the electrolytic cell can be rendered uniform, thereby permitting stable electrolysis.

Further, in the fluorine gas generating apparatus of the present invention, the above-mentioned electrolytic cell is formed from metal and serves as a cathode.

Since the electrolytic cell can be used as a cathode, there is no need to provide a separate cathode and the electrolytic cell can be miniaturized. In this manner, the fluorine gas generating apparatus can be installed in any location. For this reason, the fluorine gas generating apparatus can be installed in any required onsite location, i.e. on a production line used in a semiconductor manufacturing process.

Further, in the fluorine gas generating apparatus of the present invention, the above-mentioned electrolytic cell is formed from metal in a cylindrical shape and serves as a cathode.

The temperature regulating means can uniformly heat the electrolytic cell around its entire perimeter. In addition, since the electrode arrangement is concentrical in shape, the distribution of the electrical current inside the electrolytic cell can be rendered uniform, thereby permitting stable electrolysis. Furthermore, since the electrolytic cell can be used as a cathode, there is no need to provide a separate cathode and the electrolytic cell can be miniaturized.

Further, in the fluorine gas generating apparatus of the present invention, the above-mentioned electrolytic

cell is formed from a resin possessing resistance to corrosion by fluorine gas.

Since the electrolytic cell is formed from such a corrosion-resistant resin, the electrolytic cell is not easily corroded by the produced fluorine gas. In particular, when the amount of the generated fluorine gas is small, the electrolytic cell remains practically uncorroded. Here, resins such as trimethylpentene, tetrafluoroethylene/perfluoroalkylvinyl ether compolymers, or polytetrafluoroethylene resin and other fluorine-containing resins possessing resistance to corrosion by fluorine gas can be used as the construction material of the electrolytic cell.

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Further, in the fluorine gas generating apparatus of the present invention, the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas and has a square tubular shape.

Thus, mechanical strength can be increased even though the electrolytic cell is formed from resin.

Further, in the fluorine gas generating apparatus of the present invention, the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas in a square tubular shape, with

at least one of its side faces being in threaded engagement that permits ready opening and closing.

This allows for ready electrode replacement etc. of the electrodes or the molten salt mixture in the electrolytic cell. Further, the threaded engagement of one of the side faces can provide improved airtightness along with making it possible to increase the strength of the electrolytic cell.

In addition, in the fluorine gas generating apparatus of the present invention, the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas in a square tubular shape and at least one of its side faces is formed from a transparent resin, with the rest of its faces being formed from a fluorine-containing resin.

This allows for visual inspection of the interior of the electrolytic cell during electrolysis, such that the amount of sludge generated by the electrodes during electrolysis can be ascertained even when Ni is used for the electrodes in the electrolytic cell. Further, this allows for visual inspection of the liquid surface level of the electrolytic bath during electrolysis, which makes it possible to reliably determine the liquid surface level and

manage the liquid surface level using the liquid surface sensing means.

Additionally, in the fluorine gas generating apparatus of the present invention, there is installed a gas line used for pressurizing or depressuring the gas that passes through the above-mentioned filter and the above-mentioned gas line is provided with a pressurization or depressurization device and storage means.

Since the pressure of the fluorine gas can be set to a predetermined pressure as appropriate and, in addition, fluctuations in the liquid surface of the electrolytic bath caused by pressure fluctuations in the reaction system are prevented by the attached pressure regulating valve, the required amounts can be supplied in a stable manner.

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Brief Description of the Drawings

FIG. 1 is a schematic diagram of the fluorine gas generating apparatus of the present invention. FIG. 2 is a diagram used to explain the relationship between the operation of the pressure maintaing means installed in the electrolytic cell and the height of the liquid surface of the electrolytic bath in the electrolytic cell in a working example of the inventive fluorine gas generating apparatus. FIG. 3 is a diagram illustrating a state, in which the

liquid surface 3A of the electrolytic bath falls and 3B rises; the corresponding abnormalities are sensed by level probes 8 or 9 and solenoid valves 51, 52, 53, and 54 are closed. FIG. 4 is a diagram illustrating a state in which, subsequent to the state of FIG. 3, solenoid valve 57, which discharges gas from the anode chamber, and solenoid valve 56, which introduces gas into the cathode chamber, are opened in order to normalize the liquid surface level. FIG. 5 is a diagram illustrating a state, in which the liquid surface 3A rises and 3B falls; the corresponding abnormalities are sensed by the level probes 8 or 9, and the solenoid valves 51, 52, 53, and 54 are closed. FIG. 6 is a diagram illustrating a state in which, subsequent to the state of FIG. 5, solenoid valve 55, which introduces gas into the anode [*sic; "anode chamber"- trans.*], and solenoid valve 58, which discharges gas from the cathode chamber, are closed in order to normalize the liquid surface level. FIG. 7 is a schematic diagram illustrating another working example of the fluorine gas generating apparatus of the present invention. FIG. 8 is a perspective view illustrating an exemplary shape of a heater used in the fluorine gas generating apparatus according to the exemplary embodiment illustrated in FIG. 7.

FIG. 9 is a schematic diagram of a fluorine gas generating apparatus used in the past.

Best Mode for Carrying Out the Invention

A description of an exemplary embodiment of the present invention is given below with reference to drawings.

In FIG. 1, the reference numeral 1 designates an controlled atmosphere cabinet, 2 an electrolytic cell, 3 an electrolytic bath made up of a KF-HF type molten salt mixture, 4 a Ni anode, 5 an anode chamber, 7

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a cathode chamber, 8 a level probe serving as a liquid surface sensing means used for sensing liquid surface level abnormalities in the anode chamber 5 caused by pressure fluctuation, 9 a level probe serving as a liquid surface sensing means used for sensing liquid surface level abnormalities in the cathode chamber 7 caused by pressured fluctuations, 10 a temperature sensing means used for the electrolytic bath, 20 a cylinder used for controlling the atmosphere inside the cabinet 1, 21 a blank tower used for temporary storage of the hydrogen gas generated by the cathode, 22 an HF absorption tower filled with NaF etc. for the purspose of removing HF from the hydrogen gas, 23 a blank tower used for temporary storage of fluorine gas

generated by the anode, 24 an HF absorption tower filled with NaF etc. for the purpose of removing HF from the fluorine gas, and 25 a filter tower equipped with a filter made up of sintered Monel, sintered Hastelloy etc. for removing particles contained in the fluorine gas. In addition, gas lines 31, 40 are installed in the cabinet 1 for pressurizing or depressurizing the gas passing through the filter tower 25.

The electrolytic cell 2, which is formed from a metal such as Ni, Monel, pure iron, or stainless steel, is integrally formed in a cylindrical shape. The electrolytic cell 2 is divided into an anode chamber 5 and a cathode chamber 7 by a partition wall 28 made up of Ni or Monel. An anode 4 made up of Ni is disposed in the anode chamber 5. In addition, the electrolytic cell 2 itself serves as a cathode 6. For this reason, a bottom plate 65, which is made up of polytetrafluoroethylene etc., is attached thereto in order to prevent the mixing of the hydrogen gas generated by the cathode with the fluorine gas generated by the anode. The distance between the anode 4 and the partition wall 28 is preferably roughly equal to the distance between the partition wall 28 and the side wall of the electrolytic cell 2. In this manner, the dissolution of the partition wall 28 caused by double polarization can

be minimized, thereby producing the effect of extending the useful life of the electrolytic cell 2. The anode 4 and electrolytic cell 2, which serves as a cathode 6, are connected to a power supply 13 in order to energize them. The top cover 11 of the electrolytic cell 2 is provided with purging gas inlet and outlet ports 15, 17 for gas from the pressurized cylinder 18, which serves as a pressure maintaining means used for pressurizing the interior of the anode chamber 5 and cathode chamber 7, a generating port 16 for fluorine gas generated in the anode chamber 5, and a generating port 14 for hydrogen gas generated in the cathode chamber 7. Further, the electrolytic cell 2 is provided with a temperature regulating means for heating the interior of the electrolytic cell 2. The temperature regulating means, which comprises a heater 12 provided in intimate contact with the perimeter of the body of the electrolytic cell 2, a temperature controller (not shown) capable of providing common PID controls,

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which is connected to the heater 12 and is installed outside of the cabinet 1, and a temperature sensing means 10, such as a thermocouple, which is provided either in the anode chamber 5 or in the cathode chamber 7, regulates the temperature inside the electrolytic cell 2. It should be

noted that heat insulating material, not shown, is provided around the heater 12. While there are no particular limitations as to the shape of the heater 12, which may be a ribbon type heater, a nichrome wires, etc., shapes that embrace the entire perimeter of the electrolytic cell 2 are preferable.

Ni is used for the anode 4. As a result of using Ni for the anode 4, the admixture of CF_4 gas to the generated fluorine gas can be prevented and, in addition, no anode effects are produced. Additionally, since the electrolytic cell 2 is formed from metal such as Ni, Monel, pure iron and stainless steel, the electrolytic cell 2 can serve as the cathode 6 and the dimensions of the body of the electrolytic cell 2 can be miniaturized because there is no need to provide a separate cathode.

Further, the anode chamber 5 and cathode chamber 7 are respectively provided with a pair of long and short level probes 8 and 9, which are used for sensing the level of the liquid surface in the electrolytic bath 3. These level probes 8 and 9 are connected to a power controller, not shown, and can halt electrolysis at an upper or lower permissible level of liquid surface level fluctuation. It should be noted that while the pair of long and short level probes 8 and 9 are preferably provided in both the anode

chamber 5 and cathode chamber 7, they may be provide in either one of these chambers.

The pressure maintaining means 50, which maintains the pressure inside the anode chamber 5 and cathode chamber 7 at a level equal to or higher than a predetermined level, comprises: solenoid valves 51, 52, 53, 54, 55, 56, 57, and 58, which are opened and closed based on the sensing results obtained by the level probes 8 and 9 in order to supply gas from the pressurized cylinder 18 into the electrolytic cell 2 or discharge it therefrom; hand-operated valves 60, 61, 62,

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which are used to open and close the gas line of the pressure maintaining means 50; and flow meters 63, 64, which can be used to set the flow rate of the gas passing through the gas line to a predetermined flow rate. The pressure maintaining means is used to maintain the pressure inside the anode chamber 5 and cathode chamber 7 at a pressure that is at least 0.01 MPa higher than atmospheric pressure at all times. In this manner, the fluorine gas and hydrogen gas produced as a result of electrolysis are expelled from the electrolytic cell 2 and discharged from the respective generating ports 16, 14. Thus, the pressure maintaining means maintains the pressure inside the anode

chamber 5 and cathode chamber 7 at a level equal to or higher than a predetermined level, thereby causing the gases produced by electrolysis to be discharged from the electrolytic cell 2, and, at the same time, the entry of outside air into the electrolytic cell 2 is prevented by maintaining the pressure inside the electrolytic cell 2 at a level slightly higher than atmospheric pressure.

Futhermore, there are no particular limitations as to the gas used in the pressurized cylinder 18 so long as the gas is an inert gas. For example, when at least one rare gas selected from among Ar, Ne, Kr, Xe, etc. is used, a gas mixture of fluorine gas and these rare gases can be easily obtained in any mixing ratio. In this manner, the gas mixture can be used, for instance, as a radiation source used for lasing in an excimer laser employed in the patterning of semiconductor integrated circuits in the field of semiconductor manufacture. Installing the inventive fluorine gas generating apparatus on a production line used in the field of semiconductor manufacture allows for the fluorine gas to be appropriately supplied as needed on site.

The blank towers 21 and 23 remove the droplets of the electrolytic bath 3 contained in the fluorine gas or hydrogen gas discharged respectively from the anode chamber

5 or cathode chamber 7 during electrolysis. For this reason, the towers are preferably formed from materials possessing resistance to corrosion by fluorine gas and HF, which are exemplified, for instance, by stainless steel, Monel, Ni, fluorine-containing resins, and the like.

The absorption towers 22, 24 contain NaF and are used to remove HF contained in the discharged fluorine gas or hydrogen gas. In the same way as the blank towers 21, 23, the absorption towers 22, 24 are preferably formed from materials possessing resistance to corrosion by fluorine gas and HF, which are exemplified, for instance, by stainless steel, Monel, Ni, fluorine-containing resins, and the like.

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The filter tower 25 is installed downstream of the absorption tower 24 and is provided with a filter made up of sintered Monel or sintered Hastelloy installed inside the tower. Particles of the electrolytic bath 3, as well as complexes of iron and Ni contained in the fluorine gas discharged from the anode chamber 5, can be removed when the fluorine gas passes through the filter.

The cabinet 1, which contains the above-described equipment and ensures a controlled atmosphere, is preferably formed from materials that do not react with

fluorine gas. For example, stainless steel and other metals, as well as vinyl chloride and other resins can be used as such materials. To be able to control the atmosphere inside the cabinet 1, the cabinet 1 has an exhaust port 19 and an atmosphere control cylinder 20. This allows for controlling the atmosphere inside the cabinet 1 and producing a high purity fluorine gas. It should be noted that the cabinet 1 may incorporated into a gas cylinder cabinet used at a semiconductor manufacturing facility, etc.

The pressurizing line 40, which is installed in the cabinet 1, is provided with a pressure regulating valve 41, a pressurizing device 42, a buffer tank 44 serving as a storage means, a pressure gauge 45, a flow meter with a flow regulating capability (referred to as the "mass flow meter" below) 47, and a vacuum pump 48. The gas generated by the electrolytic cell 2 is pressurized by the pressurizing device 42. The pressure regulating valve 41 prevents the pressure inside the electrolytic cell 2 from dropping. The buffer tank 44 controls the entry and discharge of the gas using the pressure gauge 45, valves 43, 46, and the mass flow meter 47. When the fluorine gas is used, it is withdrawn from the outlet port 49.

Further, the depressurizing line 31 is provided with a pressure regulating valve 32, a buffer tank 35 serving as a reduced pressure storage means, a pressure gauge 34, and a vacuum pump 37, etc.

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The pressure inside the buffer tank 35 is controlled by the vacuum pump 37 and is adjusted using the pressure gauge 34 and valves 33 or 36, thereby controlling the entry and discharge of the fluorine gas. The pressure regulating valve 32 prevents the pressure inside the electrolytic cell 2 from dropping. When the fluorine gas is used, it is withdrawn from the outlet port 38. Thus, in the present invention, there is a provided a storage means used to store the fluorine gas generated by electrolysis, thereby producing an online fluorine gas generating apparatus that can supply the necessary amounts of fluorine gas on an as-needed basis and can be installed on a semiconductor manufacturing production line. It should be noted that the depressurizing line 31 or pressurizing line 40 can be installed as appropriate and the inventive fluorine gas generating apparatus is not limited thereto. Here, the components forming part of the lines, such as the pressurizing device 42, the pressure regulating valves 41, 32, and the buffer tanks 35, 44, are preferably formed from

materials possessing resistance to corrosion by fluorine gas. The pressurizing device 42 and pressure regulating valves 41, 32 are preferably formed from Ni, while stainless steel is suitable for the buffer tanks 35, 44 and the lines. This makes it possible to prevent corrosion etc. by the fluorine gas.

Next, the operation of the pressure maintaining means 50 and the conditions inside the electrolytic cell 2 during fluorine gas generation will be described with reference to FIGs. 2 through 6. It should be noted that, in the following drawings, the solid black valves indicate a state, in which the valves are open and the gas is flowing, while the blank valves indicate a state, in which the valves are closed and the gas is not flowing.

FIG. 2 is a diagram illustrating the open/closed state of the valves in the pressure maintaining means 50 and the state of the electrolytic bath 3 in the electrolytic cell 2 obtained during normal electrolysis. In FIG. 2, the solid black solenoid valves 51, 52, 53 and 54, hand-operated valves 60, 61, and 62, and flow meters 63 and 64 are shown as open, indicating that gas is flowing through the lines. The gas, whose flow rate is regulated by the flow meters 63 and 64, flows through the gas lines, entrained by a predetermined amount of carrier gas. Further, as shown in

FIG. 2, when the electrolysis proceeds normally, the level of the electrolytic bath 3 in the anode chamber 5 and cathode chamber 7 in the electrolytic cell 2 is the same.

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When the level of the electrolytic bath 3A in the anode chamber 5 becomes lower than the level of the electrolytic bath 3B in the cathode chamber 7 because the pressure inside the cathode chamber 7 is decreased or, in the anode chamber 5, the pressure of the anode chamber 5 is increased during electrolysis as a result of clogging of the fluorine gas lines due to accumulation of droplets from the electrolytic bath 3 etc., the abnormal liquid surface levels 3A, 3B are sensed by the level probes 8, 9 provided in the anode chamber 5 and cathode chamber 7.

As shown in FIG. 3, when this happens, the solenoid valves 51, 52, 53, and 54 are closed by control means (not shown) used for controlling the solenoid valves 51, 52, 53, 54, 55, 56, 57, and 58 in response to signals from the level probes 8 or 9, thereby stopping the flow of gas. Simultaneously, the operation of the power supply 13 used for electrolysis is halted in response to signals from the control means and the electrolysis is suspended.

When the electrolysis is halted, the solenoid valve 57 on the outlet side is opened for a short period of time and

the fluorine gas contained inside the anode chamber 5 is discharged from the fluorine gas generating port 16 provided in the top cover 11 of the electrolytic cell 2. Simultaneously, the solenoid valve 56 is also opened for a short period of time and purging gas is admitted into the cathode chamber 7 via the hydrogen gas generating port 14. This state is illustrated in FIG. 4. When the liquid surface levels of the electrolytic bath 3 in the anode chamber 5 and cathode chamber 7 are equalized again in this manner, the solenoid valves 56, 57 are closed and the solenoid valves 51, 52, 53, 54 are opened (see FIG. 2), thereby restarting the electrolysis.

Further, when the pressure inside the cathode chamber 7 is increased or when the pressure inside the anode chamber 5 is decreased as a result of clogging of the hydrogen gas line due to the accumulation of droplets of the electrolytic bath 3 etc. during electrolysis and the liquid surface level of the electrolytic bath 3 in the anode chamber 5 becomes higher than that in the cathode chamber 7, the abnormal liquid surface levels 3A or 3B of the electrolytic bath are sensed by the level probes 8, 9.

As shown in FIG. 5, when this happens, the solenoid valves 51, 52, 53, 54 are closed in response to signals from the level probes 8, 9 and the flow of gas through the

gas lines is stopped. Simultaneously, the operation of the power supply 13 used for electrolysis is stopped in response to signals from the control means and the electrolysis is halted.

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Subsequently, as shown in FIG. 6, the solenoid valve 58 is opened for a short period of time and the hydrogen gas contained inside the cathode chamber 7 is discharged from the hydrogen gas generating port 14 provided in the top cover 11 of the electrolytic cell 2. Simultaneously, the solenoid valve 55 is also opened for a short period of time and purging gas is admitted into the cathode chamber 5 via the hydrogen gas generating port 16. When the liquid surface levels of the electrolytic bath 3 in the anode chamber 5 and cathode chamber 7 are equalized again in this manner, the solenoid valves 55, 58 are closed and the solenoid valves 51, 52, 53, 54 are opened (see FIG. 2), thereby restarting the electrolysis.

As described above, control is exercised in such a manner that the solenoid valves 51, 52, 53, 54, 55, 56, 57, 58 are appropriately opened and closed in response to liquid surface sensing signals from the level probes 8, 9 provided in the anode chamber 5 and cathode chamber 7 and the liquid surface level of the electrolytic bath 3 is kept

within a predetermined range between the upper limit and lower limit of the level probes 8, 9. For this reason, the electrolysis is carried out in a stable manner, thereby making a stable supply of fluorine gas possible.

The process of fluorine gas production using the fluorine gas generating apparatus of the present embodiment will be explained next.

First, an electrolytic cell 2 is fabricated by forming a piece of stainless steel or other metal into a cylinder, such as the one illustrated in FIG. 1. Further, a top cover 11 is fabricated by providing therein gas generating ports 14, 16, purging gas inlet and outlet ports 15, 17, and an HF introduction port 26. A partition wall 28, which divides the interior of the electrolytic cell 2 into an anode chamber 5 and a cathode chamber 7, is formed in the central portion of the side of the top cover 11 that faces the electrolytic cell 2. The partition wall 28 may be formed integrally with the top cover 11 or attached thereto later by welding and the like. A Ni anode 4 is attached to the lid 11 in its central portion. In addition, a pair of long and short level probes 8, 9,

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which are used for sensing the level of the liquid surface, are attached to the anode chamber 5 and cathode chamber 7.

Furthermore, a thermocouple 10 used for regulating the temperature of the electrolytic bath 3 is attached to the cathode chamber. The electrolytic cell is then filled with particulate acid potassium fluoride (KF·HF), which forms an electrolytic bath upon heating and melting. Next, seal material is sandwiched between the top cover 11 and the electrolytic cell 2, and the top cover 11 is used to hermetically seal the electrolytic cell 2 via threaded engagement therebetween. The HF supply line is then heated to about 40°C and a predetermined amount of gaseous anhydrous hydrogen fluoride is bubbled through the charged KF·HF from the HF introduction port 26 to produce a molten KF·2HF bath. Furthermore, a heater 12, heat-insulating material, and gas lines 50 used by the pressurizing or depressurizing means are installed and housed in the cabinet 1. The amount of the HF raw material decreases with time as the electrolysis proceeds. There are two HF supply methods, including batch supply and continuous supply, with the latter being the industrially used method. The batch suppy method involves determining a reduction in the weight of the electrolytic bath 3 and supplying additional amounts of HF corresponding to the reduction. On the other hand, under the continuous supply method, a drop in the liquid surface level caused by a decrease in

the temperature of the HF in the electrolytic bath 3 is sensed by a liquid surface probe, not shown, which is attached to the cathode chamber 7, and a solenoid valve, not shown (a solenoid valve that does not sense the fluctuations in the liquid surface of the cathode chamber 7 due to pressure fluctuations), which is attached to the HF supply line, is opened, thereby automatically supplying the HF through the top cover 11. Therefore, this method consists in repeating an operational sequence, in which the liquid surface of the electrolytic bath 3 gradually rises and comes into contact with the above-mentioned liquid surface probe, not shown, at which time a signal is produced and said solenoid valve is automatically closed. It should be noted that the liquid surface level probe (not shown) provided in the cathode chamber 7 is electrically insulated from the liquid surface probe 9 disposed in the cathode chamber 7 and is designed in such a manner that when there are differential pressure fluctuations, in particular, when there is an increase in the hydrogen gas pressure in the cathode chamber 7 shown in FIG. 6, the operation of the power supply 13 is halted and, at the same time, the solenoid valves of the HF supply line are closed, thereby stopping the HF supply.

The interior of the electrolytic cell 2 is heated to approximately 90°C by the heater 12, as a result of which the KF·2HF bath is melted and can be electrolyzed.

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The fluorine gas and hydrogen gas produced by electrolysis fill in the anode chamber 5 and cathode chamber 7 and are expelled and discharged therefrom via the gas generating ports 16, 14 by the gas introduced into the chambers by the pressure maintaining means 50. The fluorine gas discharged from the anode chamber 5 passes through the blank tower 23, absorption tower 24, and filter tower 25, as a result of which it turns into particle-free high purity fluorine gas and is supplied to the pressurizing or depressurizing system.

At such time, the liquid surface levels of the electrolytic bath 3 in the anode chamber 5 and cathode chamber 7 are sensed by the level probes 8, 9 and if there is an abnormal liquid surface level, as described above, the solenoid valves 51, 52, 53, 54, 55, 56, 57, 58 are opened or closed as approprite to control the liquid surface level in the electrolytic cell 2 within a predetermined range. For this reason, stable electrolysis is continued, thereby making it possible to supply high purity fluorine gas in a stable manner.

Next, another working example of the inventive fluorine gas generating apparatus will be explained below with reference to FIG. 7 and FIG. 8. It should be noted that components identical to those of FIG. 1 through FIG. 6 are assigned the same reference numerals and their detailed descriptions are omitted.

The electrolytic cell 72 used in the fluorine gas generating apparatus of this embodiment is formed in a square tubular shape from a fluorine-containing resin, such as polytetrafluoroethylene resin, which possesses resistance to corrosion by fluorine gas and sufficient heat resistance against temperatures in the range of from 70 to 90°C during electrolysis. At least one side of the electrolytic cell 72 is formed from a tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer or from trimethylpentene resin and the like. The electrolytic cell 72 is formed by forming a cavity in a block of fluorine-containing resin to produce the integral configuration illustrated in FIG. 7, wherein the electrolytic cell 72 has a handle 73 and a partition wall 76 and can contain the electrolytic bath 3, as illustrated in FIG. 7. The electrolytic cell 72 is preferably of the shape, in which an aperture is formed in at least one side face.

A plate 75 consisting of transparent resin, such as tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer or trimethylpentene resin and the like, can hermetically seal the electrolytic cell 72 through the medium of threaded engagement with a plurality of threaded holes 74 provided in the aperture portion while permitting visual inspection of the interior of the electrolytic cell 72. At such time, in order to enhance hermeticity, it is preferable to sandwich seal material of fluorine-containing resin between the body of the electrolytic cell 72 and the plate 75. Further, a metal frame made of stainless steel etc. and of the same size as the plate 75, which consists of transparent resin such as tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer or trimethylpentene resin and the like, is applied to the seal material and threadedly engaged therewith by passings screws from above, thereby making it possible to improve the hermetic seal of the plate 75 made up of transparent resin such as tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer or trimethylpentene resin and the like, which is applied to one side of the electrolytic cell 72. Further, due to the fact that a portion of the side wall of the electrolytic cell 72 can be freely opened and closed,

the electrodes 4, 6 and the molten salt mixture constituting the electrolytic bath 3 can be easily replaced.

The electrolytic cell 72 is divided into the anode chamber 5 and cathode chamber 7 by a partition wall 76 made up of the same resin as the electrolytic cell 72, and electrodes made up of Ni are disposed therein, respectively, as the anode 4 and cathode 6. The top face of the electrolytic cell 72 is provided with purging gas inlet and outlet ports 15, 17 for gas from the pressure maintaining means 50, which pressurizes the interior of the anode chamber 5 and cathode chamber 7, a generating port 16 for fluorine gas generated in the anode chamber 5, and a generating port 14 for hydrogen gas generated in the cathode chamber 7. In addition, the electrolytic cell 72 is provided with a temperature regulating means used for heating the interior of the electrolytic cell 72. The temperature regulating means, which comprises a heater 12 provided in intimate contact with the perimeter of the body of the electrolytic cell 72, a temperature controller (not shown) capable of providing common PID control and connected to the heater 12, a thermocouple 10 provided in the cathod chamber 7, regulates the temperature inside the electrolytic cell 72. It should be noted that heat insulating material 77 is provided around the heater 12.

It should be noted that that there are no particular limitations as to the shape of the heater 12, which may be a ribbon type heater or a nichrome wire, etc. For example, a box-shaped heater, such as the one illustrated in FIG. 8, is preferred. In this manner, the electrolytic cell 72 can be housed therein and the temperature inside the electrolytic cell 72 can be precisely regulated.

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In the fluorine gas generating apparatus of the present working example, Ni is used for the anode 4 and the cathode 6. Since Ni is used for the anode 4, no CF_4 is admixed due to reactions between carbon and fluorine gas and a high purity fluorine gas can be produced. In addition, the anode effect, i.e. the polarization phenomenon, which is characteristic of carbon electrodes, can be prevented as well. Furthermore, when Ni is used for the cathode 6 as well, the hydrides and oxides generated on the surface of the Ni reduce its surface energy below that of an iron cathode, the bubbles of the generated hydrogen gas become larger and it can be prevented from mixing with the fluorine gas. Furthermore, when the anode 4 and the cathode 6 are shaped from axpanded metal or have boreholes, the mixing of the fluorine gas and hydrogen gas can be further minimized. In this manner, the distance between

the anode and cathode can be shortened, thereby permitting miniaturization of the electrolytic cell.

In the fluorine gas generating apparatus of the present working example, the electrolytic cell 72 is formed by forming a cavity in a block of fluorine-containin resin to produce the configuration illustrated in FIG. 7, wherein the cell has a handle 73, an aperture formed in one side face thereof, and a partition wall 76 formed approximately in its central portion to divide the interior of the electrolytic cell 72 in two. The gas generating ports 14, 16 and purging gas inlet and outlet ports 15, 17 are provided in the top portion along with the anode 4 and cathode 6 made of Ni. In addition, a pair of long and short level probes 8, 9, which are used for sensing the level of the liquid surface, are installed in chambers 5 and 7. The cell is then filled with particulate KF·HF. Then, a plurality of threaded holes 74 are formed in the side face of the aperture portion, after which a plate 75 made up of transparent resin such as tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer or trimethylpentene resin and the like is threadedly engaged with the opening, with seal material sandwiched therebetween. Furthermore, a thermocouple 10 used for regulating the temperature of the electrolytic bath 3 is

attached to the cathode chamber 7. A predetermined amount of anhydrous hydrogen fluoride is bubbled therethrough to prepare an electrolytic bath 3. In addition, a heater 12, heat-insulating material 77, and gas lines 50 used by the pressure maintaining means 50 are installed and housed in the cabinet.

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Then, as described above, the interior of the electrolytic cell 72 is heated to approximately 90°C by the heater 12, as a result of which the KF·2HF type salt mixture is melted and can be electrolyzed. The fluorine gas and hydrogen gas produced by electrolysis fill in the anode chamber 5 and cathode chamber 7 and are expelled and discharged therefrom via the gas generating ports 16, 14 by the gas introduced into the chambers by the pressure maintaining means 50. The fluorine gas discharged from the anode chamber 5 passes through the blank tower 23, absorption tower 24, and filter tower 25, as a result of which it is turned into and supplied as a particle-free high purity fluorine gas.

At such time, the liquid surface levels of the electrolytic bath 3 in the anode chamber 5 and cathode chamber 7 are sensed by the level probes 8, 9 and if there is an abnormal liquid surface level, as described above,

the solenoid valves 51, 52, 53, 54, 55, 56, 57, 58 are opened or closed as approprite to control the liquid surface level in the electrolytic cell 72 at a constant level. For this reason, stable electrolysis is continued, thereby making it possible to supply high purity fluorine gas in a stable manner.

When the electrolytic bath 3 is electrolyzed for an extended period of time, it gradually turns into a suspension due to the sludge, i.e. nickel fluoride (NiF_2), generated during electrolysis. However, the bath can be visually observed throught the transparent plate 75 of the electrolytic cell 72. As the NiF_2 accumulates, the resistance of the electrolytic bath 3 increases, which gradually makes it more difficult to continue the electrolysis. At such time, the electrolytic bath 3 is replaced. In addition, the electrodes are replaced when the Ni electrodes become severely worn.

As shown in FIG. 7, after bringing the high purity fluorine gas generated as described above to a predetermined pressure using the pressurizing line 40 or depressurizing line 31 provided downstream in the same manner as in FIG. 1, the gas is then stored in the buffer tank 35 etc.

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For this reason, the required amounts of fluorine gas can be supplied through the supply ports 38, 49 on an as-needed basis, and the fluorine gas generating apparatus can be installed onsite at a semiconductor manufacturing facitility. In this manner, the fluorine gas to be easily used for cleaning semiconductor products etc. Further, since the inventive fluorine gas generating apparatus is compact and can be installed onsite, there are no limitations as to its installation location. Thus, in addition to being used in a semiconductor manufacturing process, it can be used for the surface treatment of various materials. For example, it can be employed for the surface modification of paper or textiles, etc. in order to impart them with water repellency or hydrophilicity.

Industrial Applicability

The gas generating apparatus of the present invention can produce high purity fluorine gas in a stable manner. In addition, it can prevent leakage of the electrolytic bath from the electrolytic cell. In addition, it can prevent the leakage of the generated fluorine gas. Furthermore, since it can be used as an onsite fluorine generating apparatus, it eliminates the need for storing dangerous fluorine gas cylinders, as was required in the

past. In view of the above, it can be used in the field of semiconductor manufacture as well as for the surface treatment of various materials.

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CLAIMS

1. A fluorine gas generating apparatus of the present invention used for producing high purity fluorine gas by the electrolysis of a molten salt mixture containing hydrogen fluoride, which comprises: an electrolytic cell divided into an anode chamber and a cathode chamber by a partition wall, and pressure maintaining means, which supplies gas to the above-mentioned anode chamber and the above-mentioned cathode chamber, respectively, in order to maintain the interior of the above-mentioned anode chamber and the above-mentioned cathode chamber at a predetermined pressure.

2. A fluorine gas generating apparatus used for producing high purity fluorine gas by the electrolysis of a molten salt mixture containing hydrogen fluoride, which comprises: an electrolytic cell divided into an anode chamber and a cathode chamber by a partition wall; pressure maintaining means, which supplies gas to the above-mentioned anode chamber and the above-mentioned cathode chamber, respectively, in order to maintain the interior of the

above-mentioned anode chamber and the above-mentioned cathode chamber at a predetermined pressure; a controlled atmosphere cabinet housing the above-mentioned electrolytic cell; and a filter, which is housed in the above-mentioned cabinet and removes particles from the fluorine gas generated by the above-mentioned electrolytic cell.

3. The fluorine gas generating apparatus according to claim 1, wherein at least either one of the above-mentioned anode chamber and the above-mentioned cathode chamber of the above-mentioned electrolytic cell is equipped with a liquid surface sensing means for sensing the uppermost level and lowermost level of liquid level fluctuation of the molten salt.

4. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned pressure maintaining means is provided with solenoid vales which are opened and closed based on the sensing results of the liquid surface sensing means, which senses the uppermost level and lowermost level of the liquid surface fluctuation of the molten salt and is provided at least in either of the above-mentioned anode chamber and the above-mentioned cathode chamber of the above-mentioned electrolytic cell, in order to effect supply or discharge of gas to and from

the above-mentioned anode chamber and the above-mentioned cathode chamber.

5. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned molten salt mixture containing hydrogen fluoride is a KF-HF type system and the apparatus is equipped with a temperature regulating means for regulating the temperature of the above-mentioned molten salt mixture containing hydrogen fluoride.

6. The fluorine gas generating apparatus according to claim 1, wherein the gas supplied by the above-mentioned pressure maintaining means is a rare gas.

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7. The fluorine gas generating apparatus according to claim 1, wherein the anode and cathode disposed in the above-mentioned anode chamber and cathode chamber are made of nickel.

8. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned electrolytic cell is formed from metal.

9. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned electrolytic cell is cylindrical in shape.

10. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned electrolytic cell is formed from metal and serves as a cathode.

11. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned electrolytic cell is cylindrical in shape and serves as a cathode.

12. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas.

13. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas and has a square tubular shape.

14. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas in a square tubular shape and at least one side face thereof is attached via threaded engagement such that it can be freely opened and closed.

15. The fluorine gas generating apparatus according to claim 1, wherein the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas in a square tubular shape and at least one of

its side faces is formed from a transparent resin, with the rest of its faces being formed from a fluorine-containing resin.

16. The fluorine gas generating apparatus according to claim 2, wherein at least either one of the above-mentioned anode chamber and the above-mentioned cathode chamber of the above-mentioned electrolytic cell is equipped with a liquid surface sensing means for sensing the uppermost level and lowermost level of liquid level fluctuation of the molten salt.

17. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned pressure maintaining means is provided with solenoid vales which are opened and closed based on the sensing results of the liquid surface sensing means which senses the uppermost level and lowermost level of the liquid surface fluctuation of the molten salt and is provided at least in either of the above-mentioned anode chamber and the above-mentioned cathode chamber of the above-mentioned electrolytic cell, in order to effect supply or discharge of gas to and from the above-mentioned anode chamber and the above-mentioned cathode chamber.

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18. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned molten salt mixture containing hydrogen fluoride is a KF-HF type system and the apparatus is equipped with a temperature regulating means for regulating the temperature of the above-mentioned molten salt mixture containing hydrogen fluoride.

19. The fluorine gas generating apparatus according to claim 2, wherein the gas supplied by the above-mentioned pressure maintaining means is a rare gas.

20. The fluorine gas generating apparatus according to claim 2, wherein the anode and cathode disposed in the above-mentioned anode chamber and cathode chamber are made of nickel.

21. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned electrolytic cell is formed from metal.

22. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned electrolytic cell is cylindrical in shape.

23. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned electrolytic cell is formed from metal and serves as a cathode.

24. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned electrolytic cell is cylindrical in shape and serves as a cathode.

25. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas.

26. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas and has a square tubular shape.

27. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas in a square tubular shape and at least one side face thereof is attached via threaded engagement such that it can be freely opened and closed.

28. The fluorine gas generating apparatus according to claim 2, wherein the above-mentioned electrolytic cell is formed from a resin possessing resistance to corrosion by fluorine gas in a square tubular shape and at least one of its side faces is formed from a transparent resin, with the rest of its faces being formed from a fluorine-containing resin.

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29. The fluorine gas generating apparatus according to claim 2, wherein there are installed gas lines used to pressurize or depressurize gas passing through the above-mentioned filter and the above-mentioned gas lines are provided with pressurizing or depressurizing devices and storage means.

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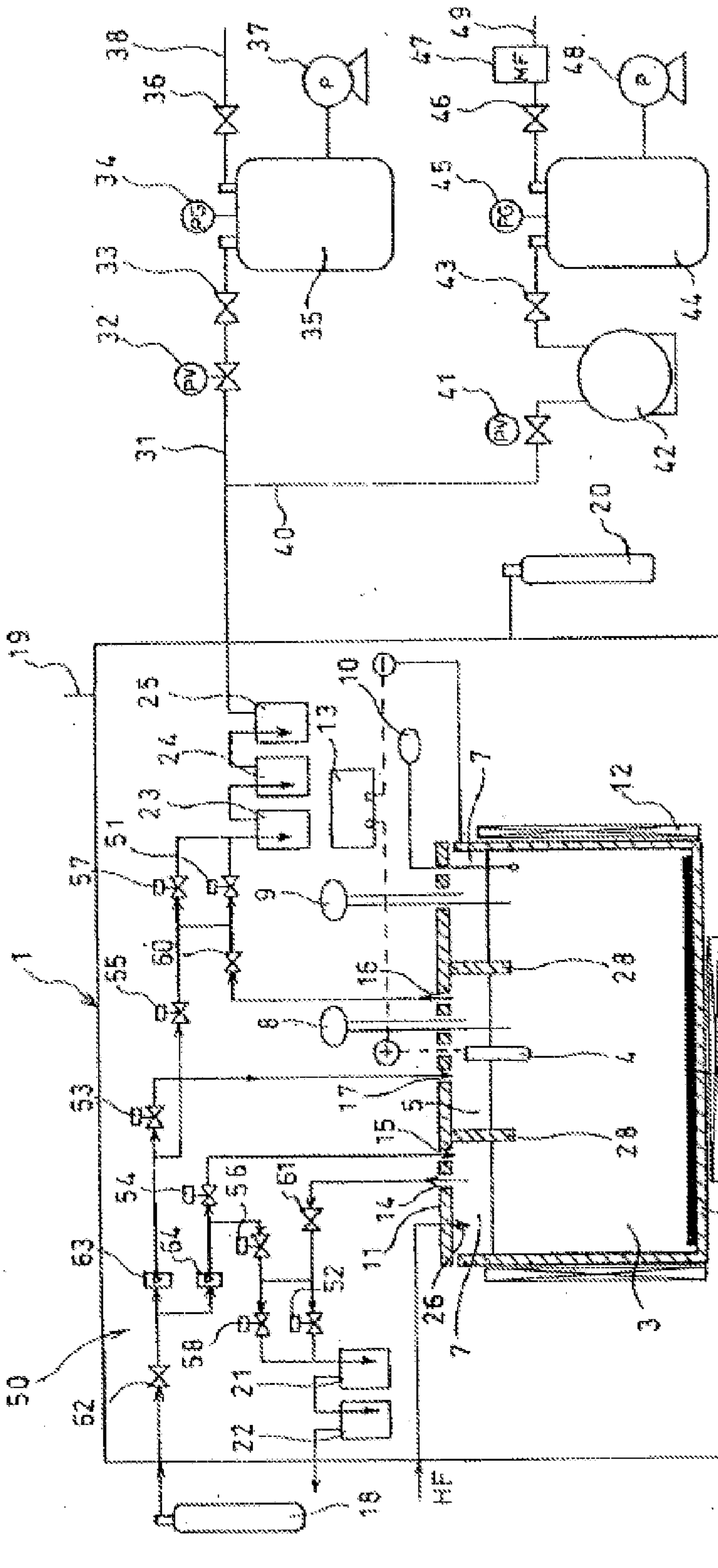
第　1　図



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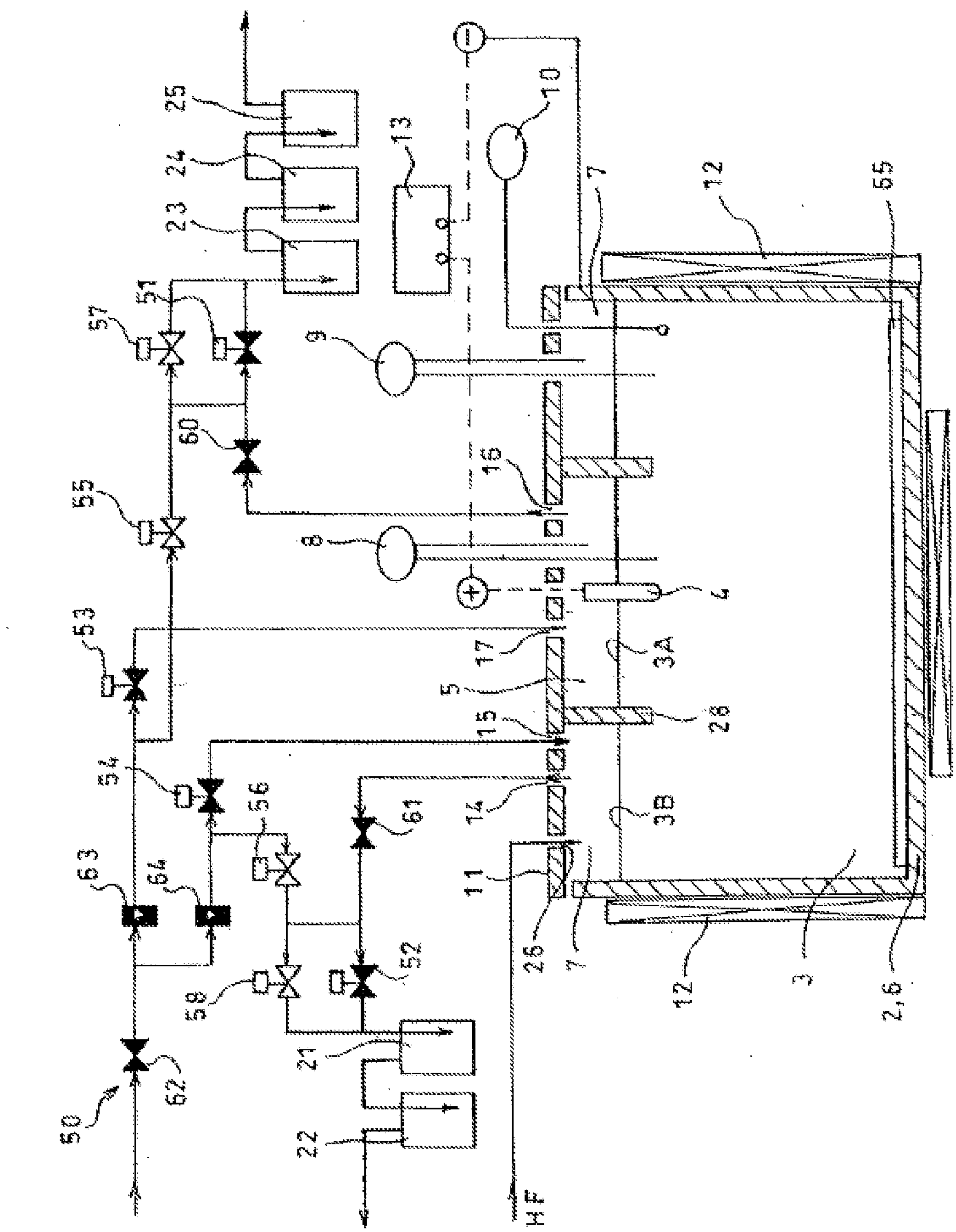
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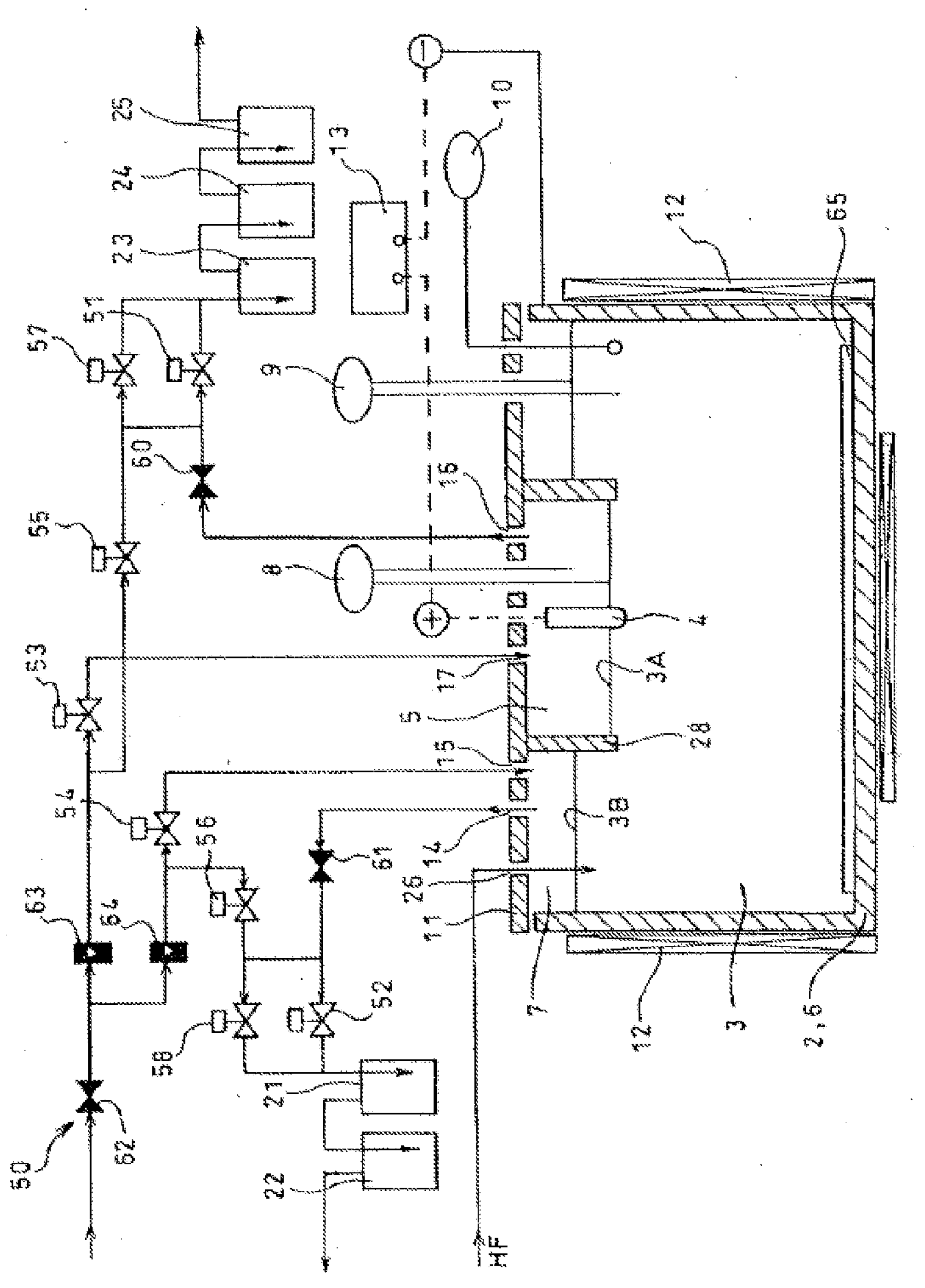
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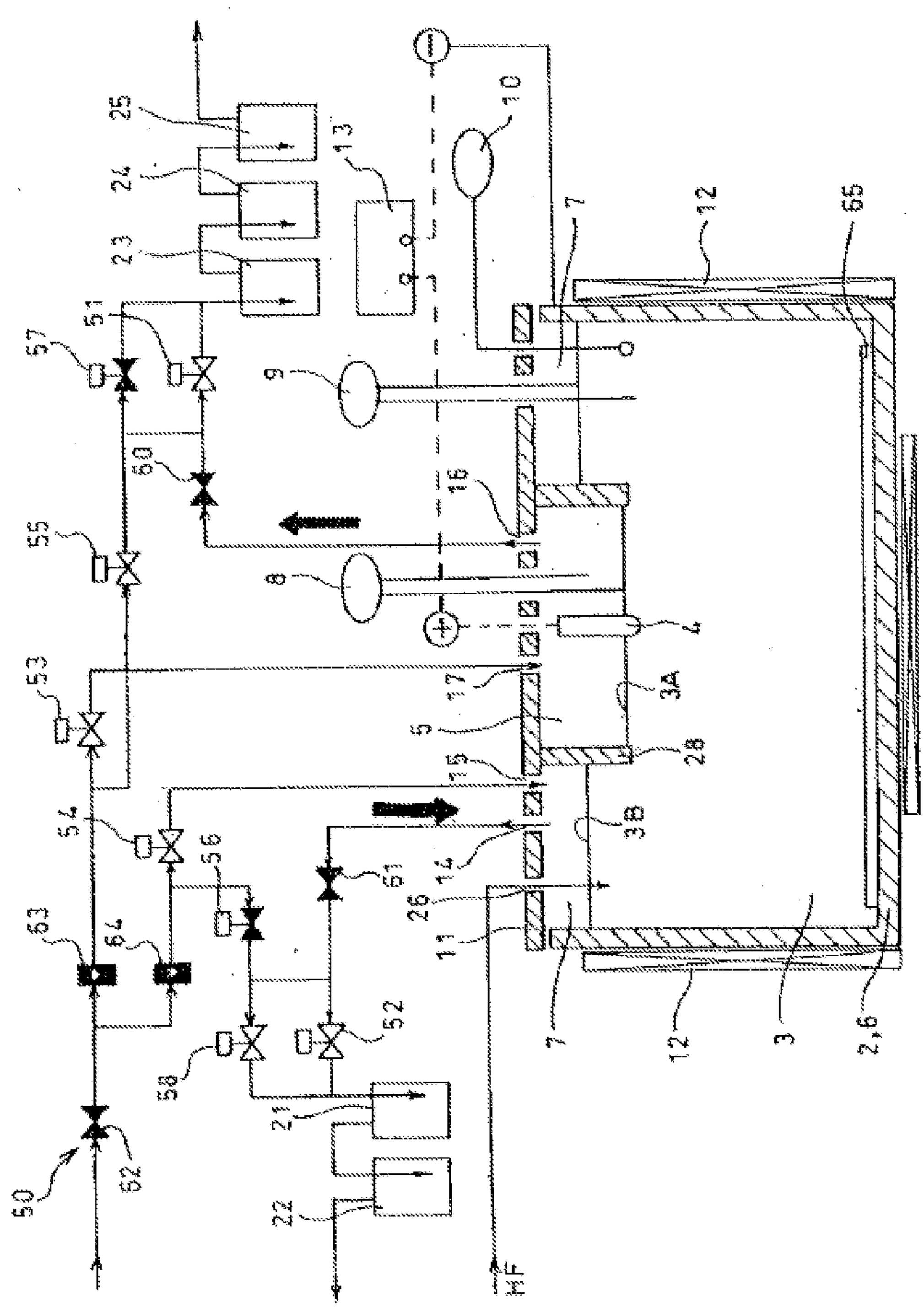
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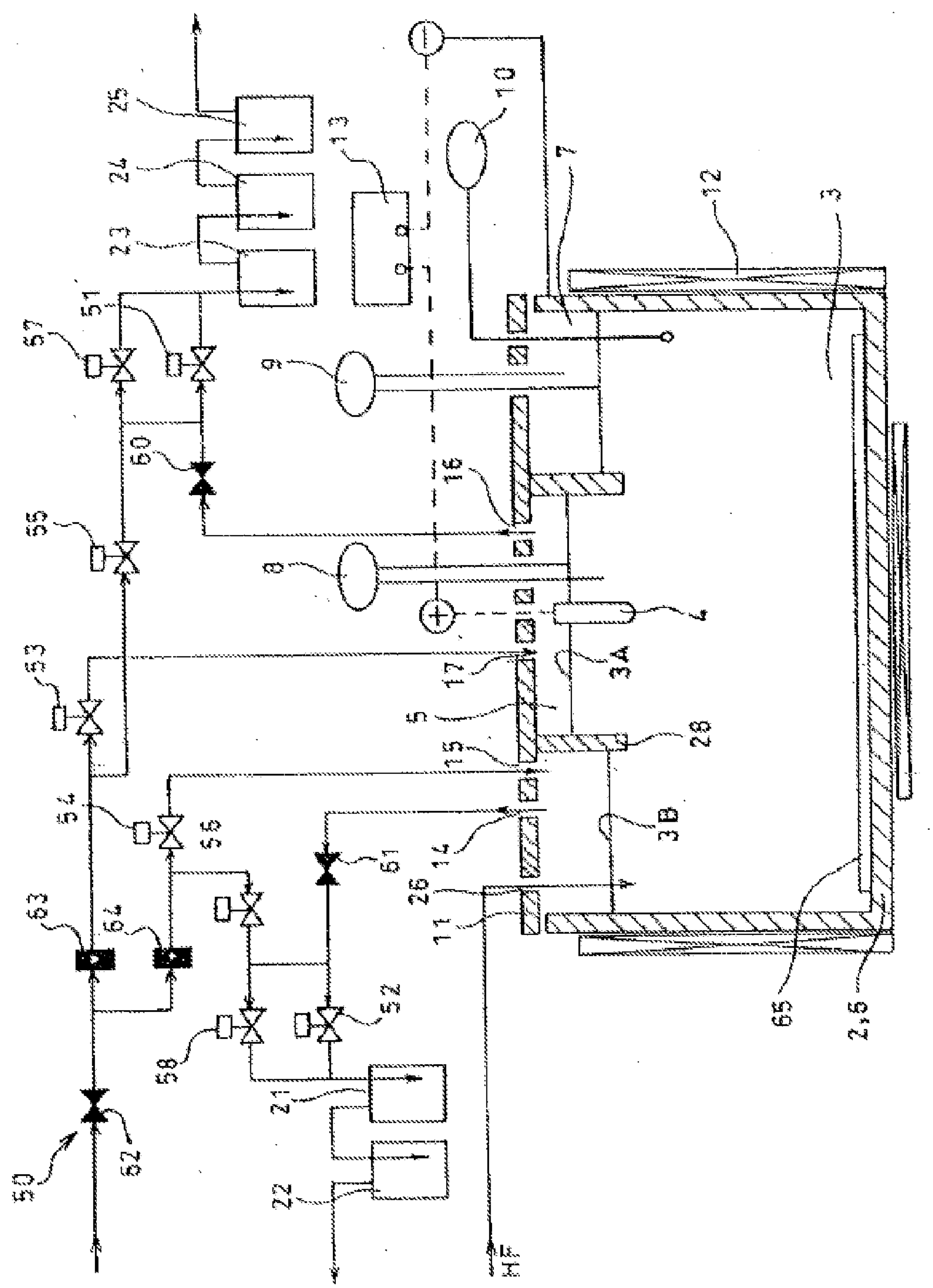

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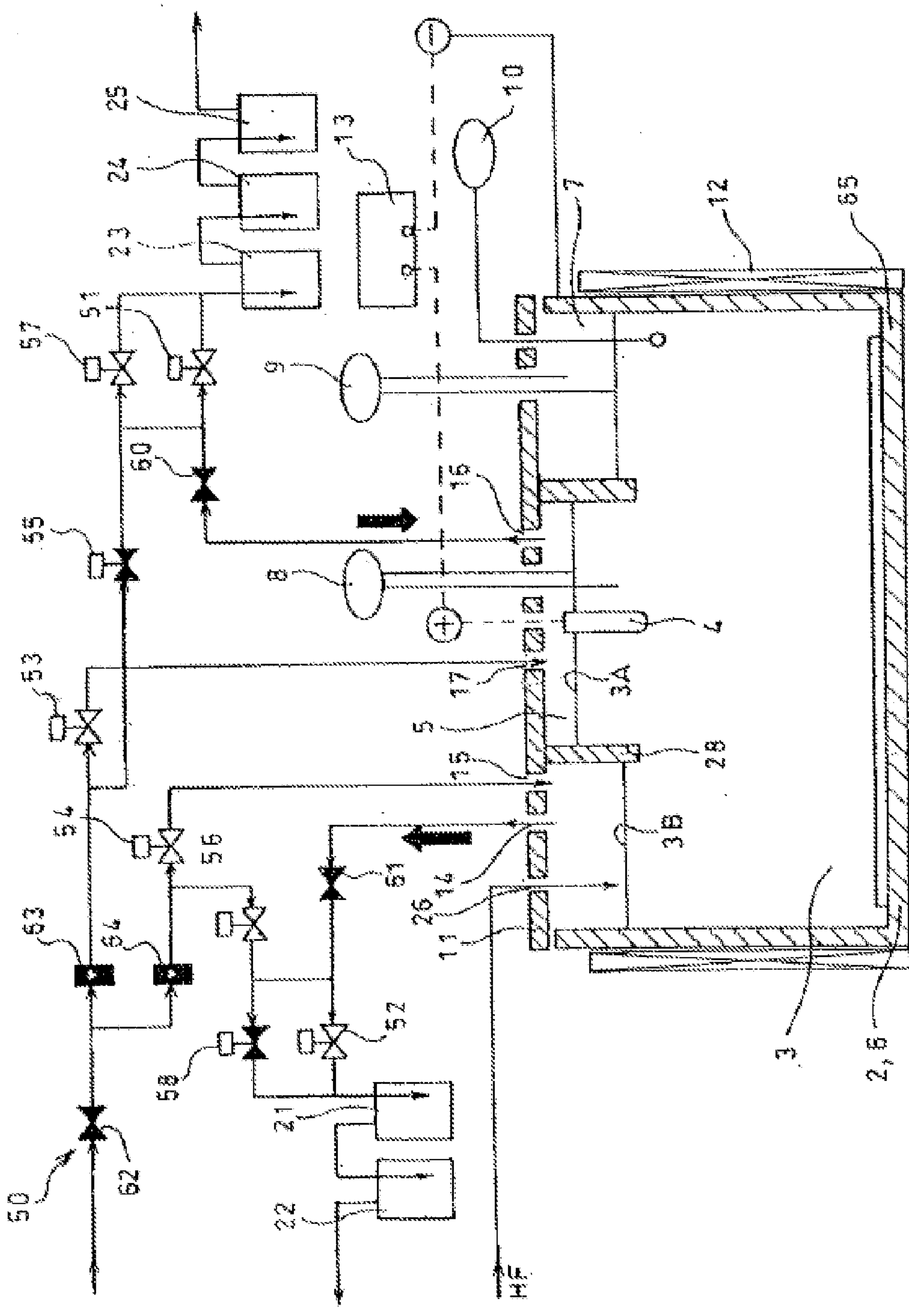

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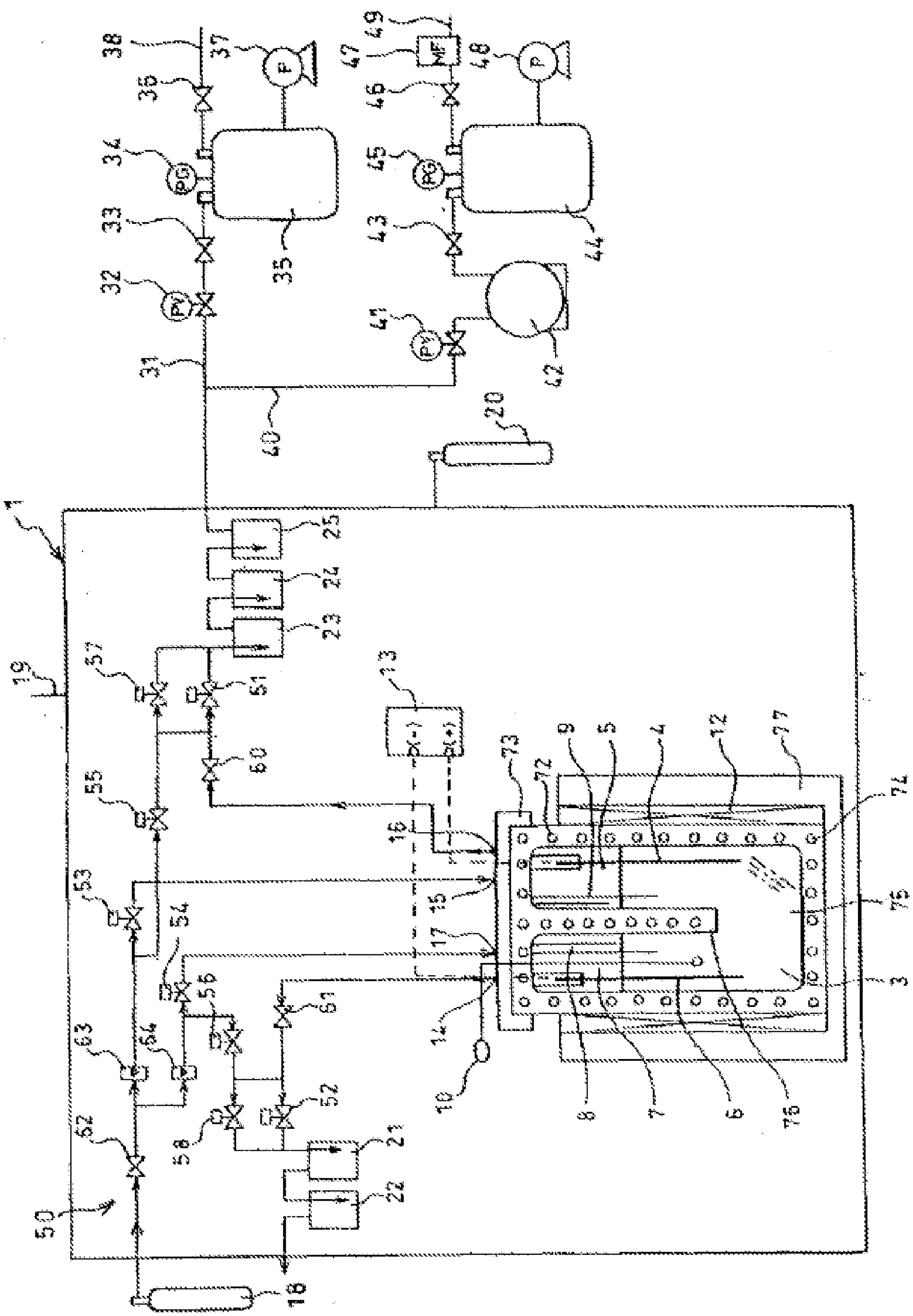

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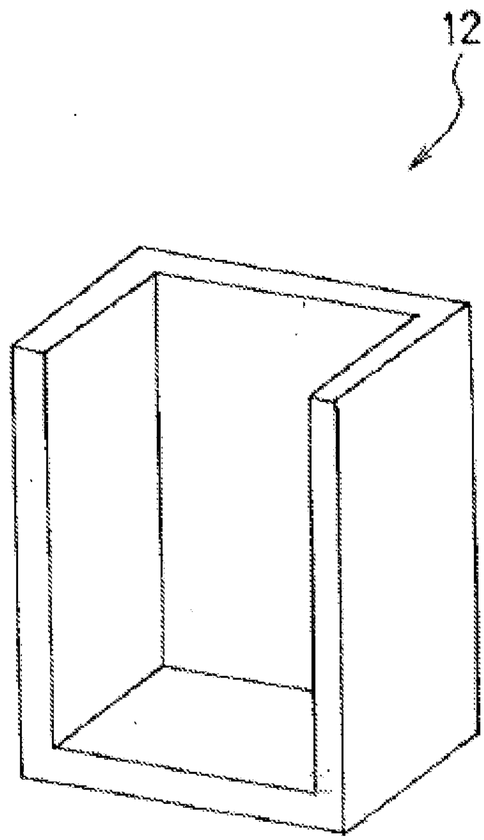

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